

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 128 446 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
29.08.2001 Bulletin 2001/35

(51) Int Cl.7: **H01L 33/00**

(21) Application number: **01301628.2**

(22) Date of filing: **22.02.2001**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **23.02.2000 JP 2000045318**

(71) Applicant: **Riken**
Wako-shi, Saitama 351-0198 (JP)

(72) Inventors:
• **Hirayama, Hideki**
Wako-shi, Saitama, 351-0198 (JP)
• **Aoyagi, Yoshinobu**
Wako-shi, Saitama, 351-0198 (JP)

(74) Representative:
Cross, Rupert Edward Blount et al
BOULT WADE TENNANT,
Verulam Gardens
70 Gray's Inn Road
London WC1X 8BT (GB)

(54) **InAlGaN emitting light in ultraviolet short-wavelength region and process for preparing the same as well as ultraviolet light-emitting device using the same**

(57) For the purpose of emitting light in an ultraviolet short-wavelength region having a wavelength of 360 nm or shorter, it is arranged in InAlGaN in such that a ratio

of composition of In is 2% to 20%, a ratio of composition of Al is 10% to 90%, and a total of ratios of composition in In, Al, and Ga is 100%.

EP 1 128 446 A2

Description

Background of the Invention

Field of The Invention

[0001] The present invention relates to InAlGa_N (indium aluminum gallium nitride) emitting light in an ultraviolet short-wavelength region, and a process for preparing the same as well as to an ultraviolet light-emitting device using the InAlGa_N emitting light in an ultraviolet short-wavelength region, and more particularly to InAlGa_N emitting light in an ultraviolet short-wavelength region at room temperature with high efficiency, and a process for preparing the same as well as to an ultraviolet light-emitting device using the InAlGa_N emitting light in an ultraviolet short-wavelength region at room temperature with high efficiency.

Description of The Related Art

[0002] Nitride semiconductors such as GaN (gallium nitride), InGa_N (indium gallium nitride), and AlGa_N (aluminum gallium nitride) which have been heretofore utilized as an ultraviolet light-emitting device for emitting light in an ultraviolet short-wavelength region having a wavelength of 360 nm or shorter. However, highly efficient light emission cannot be attained by such nitride semiconductors at room temperature in an ultraviolet short-wavelength having a wavelength of 360 nm or less. Accordingly, it has been concluded that an ultraviolet light-emitting device, which can emit light in an ultraviolet short-wavelength region cannot be realized by the use of such nitride semiconductors as described above.

[0003] Namely, a wavelength of up to 370 nm can be merely realized with respect to light-emitting diode as a light-emitting device wherein a nitride semiconductor is used in a short-wavelength, while only a wavelength of up to 390 nm can be realized with respect to laser diode until now.

[0004] Thus, there has been a strong need for developments as to InAlGa_N exhibiting highly efficient light emission at room temperature in an ultraviolet short-wavelength region of a wavelength of 360 nm or shorter, and a process for preparing the same as well as an ultraviolet light-emitting device wherein the InAlGa_N emitting light in an ultraviolet short-wavelength region is employed.

Objects and Summary of The Invention

[0005] The present invention has been made in view of the needs which have been heretofore demanded strongly as described above, and an object of the invention is to provide InAlGa_N exhibiting highly efficient light emission at room temperature in an ultraviolet short-wavelength region of a wavelength of 360 nm or shorter,

and a process for preparing the same as well as an ultraviolet light-emitting device wherein the InAlGa_N emitting light at room temperature with high efficiency in an ultraviolet short-wavelength region is used.

5 [0006] In order to achieve the above-described object, InAlGa_N according to the invention comprises a ratio of composition of In being 2% to 20%, a ratio of composition of Al being 10% to 90%, and a total of ratios of composition of In, Al, and Ga being 100%.

10 [0007] Furthermore, a ratio of composition of the In may be 6% or more in the above described InAlGa_N.

[0008] Moreover, a process for preparing InAlGa_N according to the present invention comprises the InAlGa_N being subjected to crystal growth at a growth temperature of 830°C to 950°C in accordance with metalorganic vapor phase epitaxy wherein ammonia, trimethylgallium, a trimethylindium adduct, and trimethylaluminum are used as material gases.

15 [0009] Furthermore, a flow rate of the ammonia is 2 L/min, a flow rate of the trimethylgallium is 2 μmol/min to 5 μmol/min, a flow rate of the trimethylindium adduct is 5 μmol/min to 60 μmol/min, and a flow rate of the trimethylaluminum is 0.5 μmol/min to 10 μmol/min in the above described process for preparing InAlGa_N according to the invention.

25 [0010] Moreover, an ultraviolet light-emitting device using the InAlGa_N according to the invention comprises a first InAlGa_N layer wherein a ratio of composition of In is 2% to 20%, a ratio of composition of Al is 10% to 90%, and a total of ratios of composition in In, Al, and Ga is 100%, and a second InAlGa_N layer ratios of composition of which differ from that of the first layer wherein a ratio of composition of In is 2% to 20%, a ratio of composition of Al is 10% to 90%, and a total of ratios of composition in In, Al, and Ga is 100%; and the InAlGa_N involves a quantum well structure formed by laminating alternately a plurality of layers of the first InAlGa_N layer, and the second InAlGa_N layer.

30 [0011] Furthermore, a ratio of composition of the In in the first InAlGa_N layer is 6% or more in the above described ultraviolet light-emitting device using the InAlGa_N according to the present invention.

Brief Description of The Drawings

45 [0012] The present invention will become more fully understood from the detailed description given herein and the accompanying drawings which are given by way of illustration only, and thus are not limitative of the present invention, and wherein:

50 FIG. 1 is an explanatory diagram illustrating a conceptual construction of crystal growth equipment for producing InAlGa_N emitting light in an ultraviolet short-wavelength region according to the present invention on a substrate such as a semiconductor wafer as a crystal thin film in accordance with metalorganic vapor phase epitaxy;

FIG. 2 is a correlated diagram of growth temperatures and gas flows;

FIG. 3 is an explanatory diagram showing a range of growth temperature in vapor phase deposition of a nitride semiconductor;

FIG. 4 is a graphical representation indicating effects in introduction of Al into InGa_N;

FIG. 5 is a graphical representation indicating effects in introduction of In into AlGa_N;

FIG. 6 is a graphical representation indicating ultraviolet light emission from a quantum well of InAlGa_N; and

FIG. 7 is an explanatory view illustrating a quantum well structure formed by laminating InAlGa_N on SiC through an AlGa_N buffer layer.

Detailed Description of The Preferred Embodiments

[0013] In the following, an example of embodiments of InAlGa_N emitting light in an ultraviolet short-wavelength region according to the present invention, and a process for preparing the same as well as of an ultraviolet light-emitting device wherein the InAlGa_N emitting light in an ultraviolet short-wavelength region is used will be described in detail.

[0014] InAlGa_N emitting light in an ultraviolet short-wavelength region according to the present invention (hereinafter referred optionally to as "ultraviolet light-emitting InAlGa_N") may be prepared on a substrate as a semiconductor wafer as a crystal thin film by crystal growth equipment in accordance with, for example, metalorganic vapor phase epitaxy. In FIG. 1, an example of such crystal growth equipment is illustrated.

[0015] Namely, FIG. 1 is an explanatory diagram illustrating a conceptual construction of crystal growth equipment for preparing ultraviolet light-emitting InAlGa_N wherein the crystal growth equipment 10 is provided with a crystal growth reactor 14 around which is surrounded by an RF heating coil 12 wherein a susceptor 18 on the upper surface of which is placed a semiconductor wafer 16 as a substrate for growing the ultraviolet light-emitting InAlGa_N, and the susceptor that functions to heat the semiconductor wafer 16.

[0016] Furthermore, an RF power source 20 is connected to the RF heating coil 12, and in addition, an RF controller 22 composed of a microcomputer is connected to the RF power source.

[0017] The RF controller 22 controls an output of the RF power source 20. Namely, power supply from the RF power source 20 to the RF heating coil 12 is controlled by the RF controller 22, and the susceptor 18 is heated by the RF heating coil 12 in response to the power supply from the RF power supply source 20.

[0018] More specifically, the susceptor 18 is heated by eddy-current induction heating due to power supply from the RF power source 20 to the RF heating coil 12 in the crystal growth equipment 10.

[0019] The susceptor 18 is made of, for example, car-

bon and the like.

[0020] On one hand, on the crystal growth reactor 14 are defined a gas introducing hole 14a for introducing a variety of gases such as material gases of materials of ultraviolet light-emitting InAlGa_N to be formed on the semiconductor wafer 16 and carrier gases as well as a gas exhausting hole 14b for exhausting a variety of gases which have been introduced in the crystal growth reactor 14.

[0021] In the construction as described above, material gases of materials required for forming a crystal thin film of ultraviolet light-emitting InAlGa_N are introduced in the crystal growth reactor 14, which has been depressurized to 76 Torr, together with carrier gases through the gas introducing hole 14a in order to form the crystal thin film of the ultraviolet light-emitting InAlGa_N on the semiconductor wafer 16 placed on the susceptor 18.

[0022] In this case, the susceptor 18 has been heated by the RF heating coil 12 in response to power supply from the RF power source 20 that is controlled by the RF controller 22 based on a monitor of a thermocouple (not shown), which had been embedded in the susceptor 18, so that the semiconductor wafer 16 is also heated by means of heat conduction derived from the susceptor 18 heated at a growth temperature optimum for forming the crystal thin film of the ultraviolet light-emitting InAlGa_N in accordance with crystal growth.

[0023] Thus, the material gases introduced in the crystal growth reactor 14 are decomposed and reacted by heat, whereby the crystal thin film of the ultraviolet light-emitting InAlGa_N is formed on the semiconductor wafer 16 in accordance with crystal growth.

[0024] In this case, the material gases required for forming a crystal thin film of ultraviolet light-emitting InAlGa_N are ammonia, trimethylgallium, a trimethylindium adduct, and trimethylaluminum. Furthermore, the carrier gases are hydrogen and nitrogen.

[0025] A flow rate of these material gases is, for example, 2 L/min in case of ammonia, 2 μmol/min to 5 μmol/min in case of trimethylgallium, 5 μmol/min to 60 μmol/min in case of trimethylindium adduct, and 0.5 μmol/min to 10 μmol/min in case of trimethylaluminum, respectively.

[0026] On one hand, a flow rate of the carrier gases is 100 cc/min in case of hydrogen, and 2 L/min in case of nitrogen, respectively.

[0027] Since a growth temperature of crystal growth of ultraviolet light-emitting InAlGa_N is 830°C to 950°C, the semiconductor wafer 16 is set in such that it is heated at a temperature of 830°C to 950°C.

[0028] Furthermore, a growth rate of the crystal thin film of ultraviolet light-emitting InAlGa_N is set at 120 nm/hour.

[0029] FIG. 2 is a correlated diagram of growth temperatures and gas flows. The material gases are fed into the crystal growth reactor 14 at timings and growth temperatures as shown in FIG. 2.

[0030] Meanwhile, a growth temperature in crystal

growth of InGa_N is within a range of from 650°C to 750°C as shown in FIG. 3, while a growth temperature in crystal growth of AlGa_N is within a range of from 1000°C to 1200°C as shown in FIGS. 2 and 3. In this respect, InGa_N differs remarkably from AlGa_N in their growth temperatures in crystal growth. Therefore, it has been heretofore considered that preparation of high quality crystal of InAlGa_N is impossible.

[0031] According to experiments by the present inventor, however, results of the experiments have exhibited that crystal growth of high quality InAlGa_N proceeds at a temperature of 830°C to 950°C being an intermediate temperature defined between the growth temperature in crystal growth of InGa_N and the growth temperature in crystal growth of AlGa_N, whereby ultraviolet light-emitting InAlGa_N can be obtained as shown in FIGS. 2 and 3.

[0032] In a ratio of composition of the resulting ultraviolet light-emitting InAlGa_N thus obtained, In is 2% to 20%, and Al is 10% to 90% (It is to be noted that total in ratios of composition of In, Al, and Ga is 100%). In this case, it is preferred that a ratio of composition of In is 6% or higher.

[0033] In vapor phase deposition of the above described ultraviolet light-emitting InAlGa_N, a content of In in a crystal increases inductively by introduction of Al as mentioned hereinafter by referring to FIGS. 4 through 6.

[0034] As a result of introduction of several % of In into AlGa_N, ultraviolet light-emitting intensity is remarkably enhanced.

[0035] Namely, ultraviolet light-emitting InAlGa_N is possible to emit light at room temperature with high efficiency in a short-wavelength region in a deep ultraviolet region of a wavelength of 280 nm to 360 nm. Accordingly, when such ultraviolet light-emitting InAlGa_N as described above is used, an ultraviolet light-emitting device emitting light in a wavelength region of a wavelength of 280 nm to 360 nm can be prepared.

[0036] In the following, experimental results of ultraviolet light-emitting InAlGa_N at room temperature will be described by referring to FIGS. 4 through 6 wherein the ultraviolet light-emitting InAlGa_N was prepared at 830°C growth temperature and at 120 nm/hour growth rate in the case where a flow rate of ammonia is 2 L/min, that of trimethylgallium is 3 μmol/min, that of a trimethylindium adduct is 60 μmol/min, and that of trimethylaluminum is 0.5 μmol/min with respect to material gases, besides a flow rate of hydrogen is 100 cc/min, and that of nitrogen is 2 L/min with respect to carrier gases.

[0037] FIG. 4 indicates an effect of introduction of Al into InGa_N. As shown in FIG. 4, In is introduced inductively into a crystal as a result of introduction of Al into InGa_N. In this connection, the most intensive light emission is achieved in the case when In is 6%, and Al is 16% in a ratio of composition of InGa_N.

[0038] Furthermore, FIG. 5 indicates an effect of introduction of In into AlGa_N. Light-emitting intensity in-

creases remarkably with increase of a ratio of introduction of In into AlGa_N as shown in FIG. 5.

[0039] Moreover, FIG. 6 indicates results of ultraviolet light emission in the case where an InAlGa_N layer having a different ratio of composition is laminated on SiC through an AlGa_N buffer layer to form a quantum well structure as shown in FIG. 7, and it is irradiated with laser beam of 257 nm wavelength.

[0040] As described above, since InAlGa_N emits ultraviolet light with a quantum well structure, an ultraviolet light-emitting device such as light-emitting diode, and laser diode provided with a quantum well structure that is prepared by laminating InAlGa_N layers having different ratios of composition from one another can be constructed.

[0041] More specifically, a quantum well structure may be constructed by such a manner that InAlGa_N layers formed on SiC through a buffer layer of AlGa_N are doped in the form of p-type or n-type, and they are laminated on one another to form the quantum well structure as shown in FIG. 7, thereafter it is provided with electrodes.

[0042] The present invention is constructed as described above, so that it exhibits such an excellent advantage to provide InAlGa_N emitting light at room temperature with high efficiency in an ultraviolet short-wavelength region of a wavelength of 360 nm or shorter, and a process for preparing the same as well as an ultraviolet light-emitting device using the InAlGa_N emitting light in an ultraviolet short-wavelength region.

[0043] It will be appreciated by those of ordinary skill in the art that the present invention can be embodied in other specific forms without departing from the spirit or essential characteristics thereof.

[0044] The presently disclosed embodiments are therefore considered in all respects to be illustrative and not restrictive. The scope of the invention is indicated by the appended claims rather than the foregoing description, and all changes that come within the meaning and range of equivalents thereof are intended to be embraced therein.

[0045] The entire disclosure of Japanese Patent Application No. 2000-45318 filed on February 23, 2000 including specification, claims, drawings and summary are incorporated herein by reference in its entirety.

Claims

1. InAlGa_N emitting light in an ultraviolet short-wavelength region, comprising:
a ratio of composition of In being 2% to 20%,
a ratio of composition of Al being 10% to 90%, and
a total of ratios of composition of In, Al, and Ga being 100%.
2. The InAlGa_N emitting light in an ultraviolet short-wavelength region as claimed in claim 1 wherein a

ratio of composition of In is 6% or more.

3. A process for preparing InAlGa_N emitting light in an ultraviolet short-wavelength region, comprising:
the InAlGa_N being subjected to crystal growth at a growth temperature of 830°C to 950°C in accordance with metalorganic vapor phase epitaxy wherein ammonia, trimethylgallium, a trimethylindium adduct, and trimethylaluminum are used as material gases.
 - 5
 - 10
4. The process for preparing InAlGa_N emitting light in an ultraviolet short-wavelength region as claimed in claim 3 wherein a flow rate of the ammonia is 2 L/min, a flow rate of the trimethylgallium is 2 μmol/min to 5 μmol/min, a flow rate of the trimethylindium adduct is 5 μmol/min to 60 μmol/min, and a flow rate of the trimethylaluminum is 0.5 μmol/min to 10 μmol/min.
 - 15
 - 20
5. An ultraviolet light-emitting device using InAlGa_N emitting light in an ultraviolet short-wavelength region, comprising:
a first InAlGa_N layer wherein a ratio of composition of In is 2% to 20%, a ratio of composition of Al is 10% to 90%, and a total of ratios of composition in In, Al, and Ga is 100%;
a second InAlGa_N layer ratios of composition of which differ from that of said first layer wherein a ratio of composition of In is 2% to 20%, a ratio of composition of Al is 10% to 90%, and a total of ratios of composition in In, Al, and Ga is 100%; and
involving a quantum well structure formed by laminating alternately a plurality of layers of said first InAlGa_N layer, and said second InAlGa_N layer.
 - 25
 - 30
 - 35
6. The ultraviolet light-emitting device using InAlGa_N emitting light in an ultraviolet short-wavelength region as claimed in claim 5 wherein a ratio of composition of the In in said first InAlGa_N layer is 6% or more.
 - 40
 - 45
 - 50
 - 55

FIG. 1

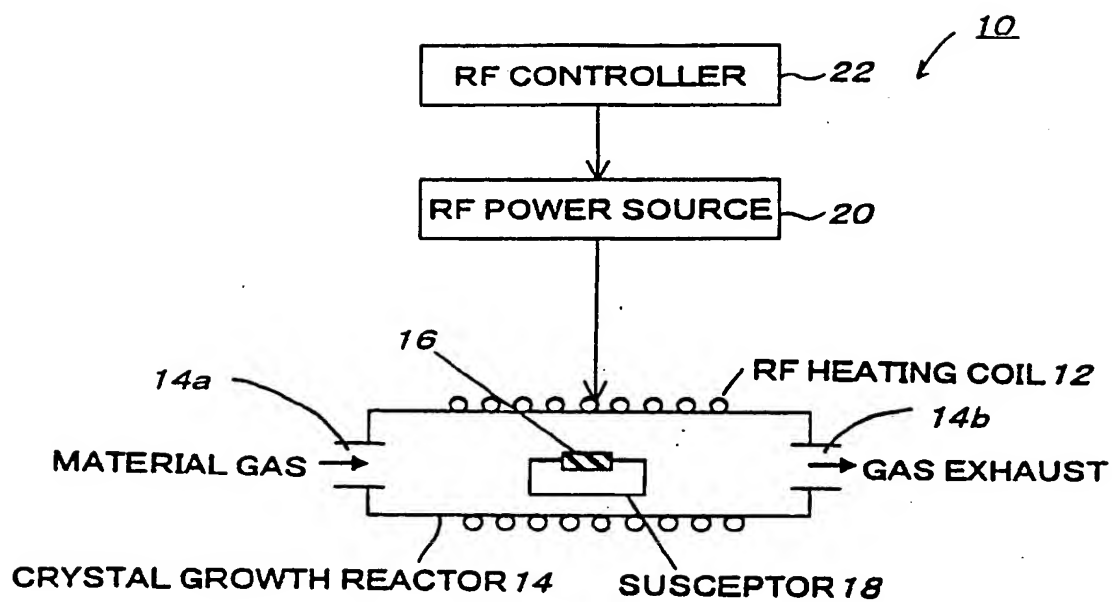


FIG. 2

CORRELATED DIAGRAM OF GROWTH TEMPERATURES AND GAS FLOWS

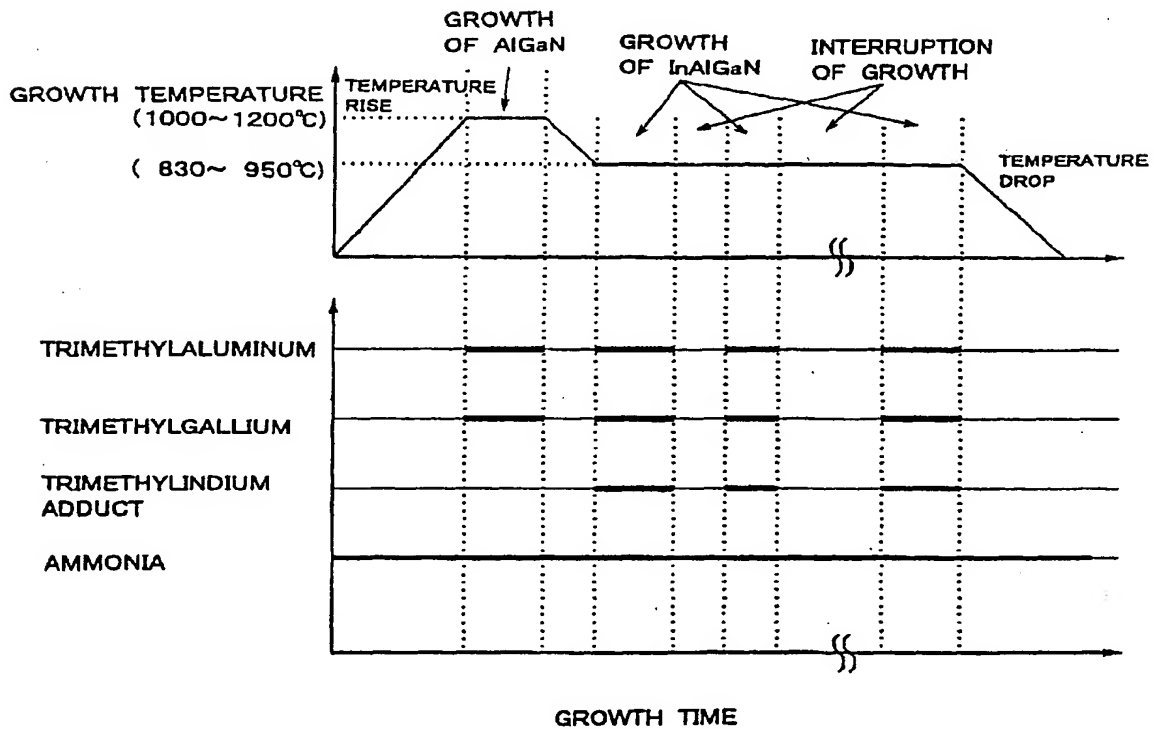


FIG. 3

GROWTH TEMPERATURE RANGE IN METALORGANIC
VAPOR PHASE EPITAXY OF NITRIDE SEMICONDUCTOR

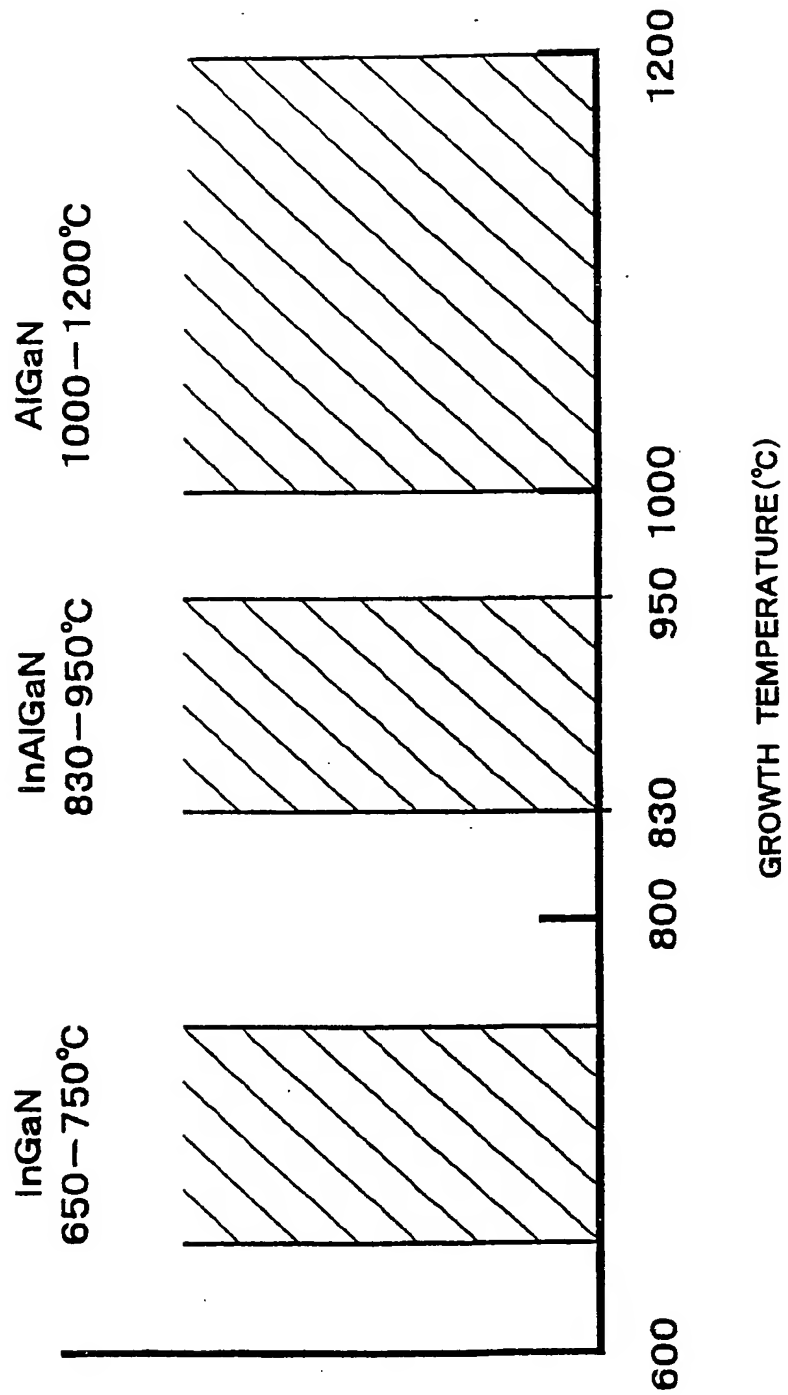


FIG. 4

EFFECT OF ADDING Al TO InGaN

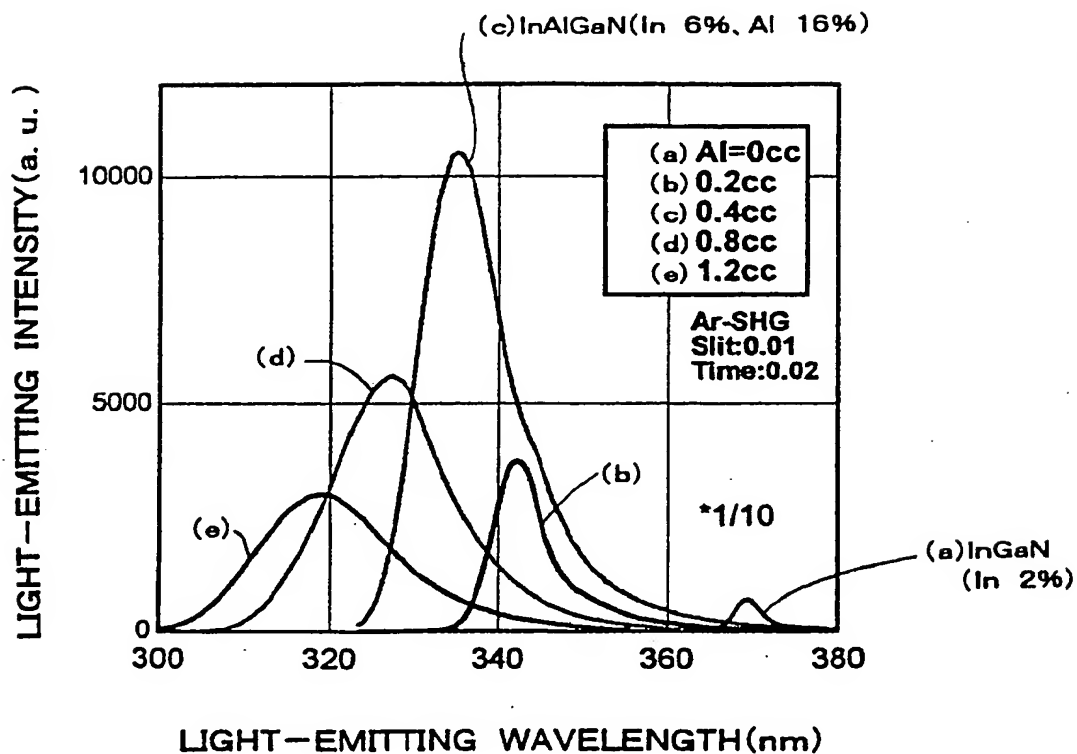


FIG. 5

EFFECT OF INTRODUCTION OF In INTO AlGaN

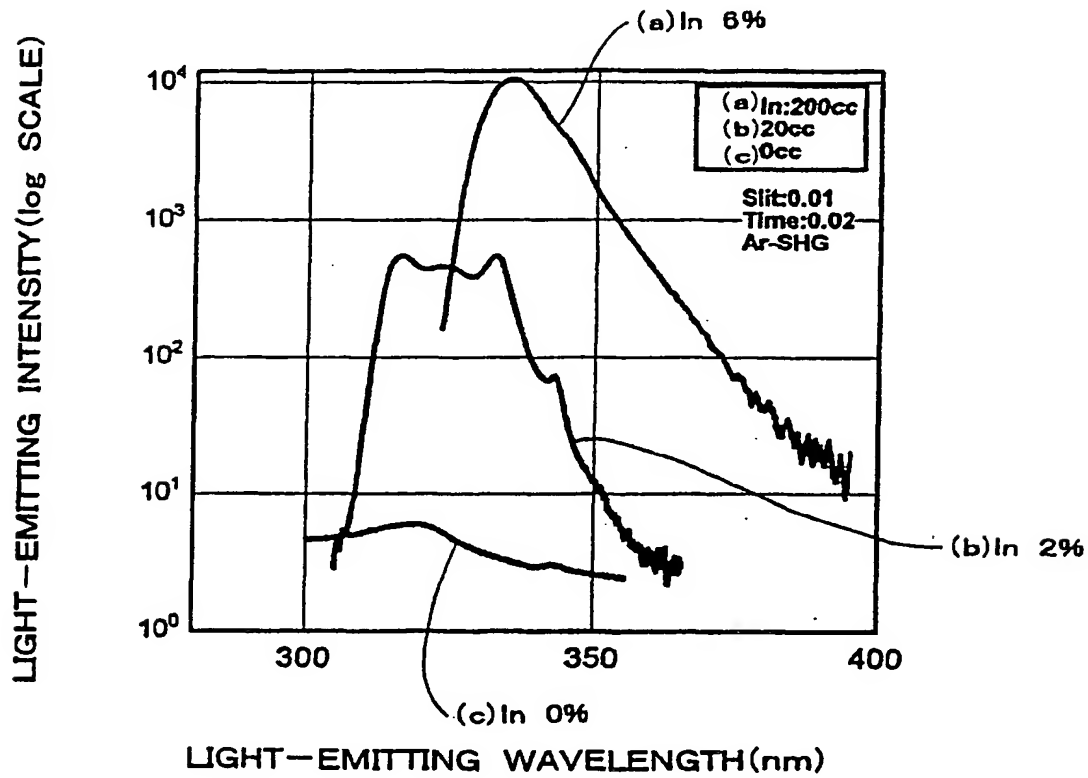


FIG. 6

ULTRAVIOLET LIGHT EMISSION FROM InAlGa_N QUANTUM WELL

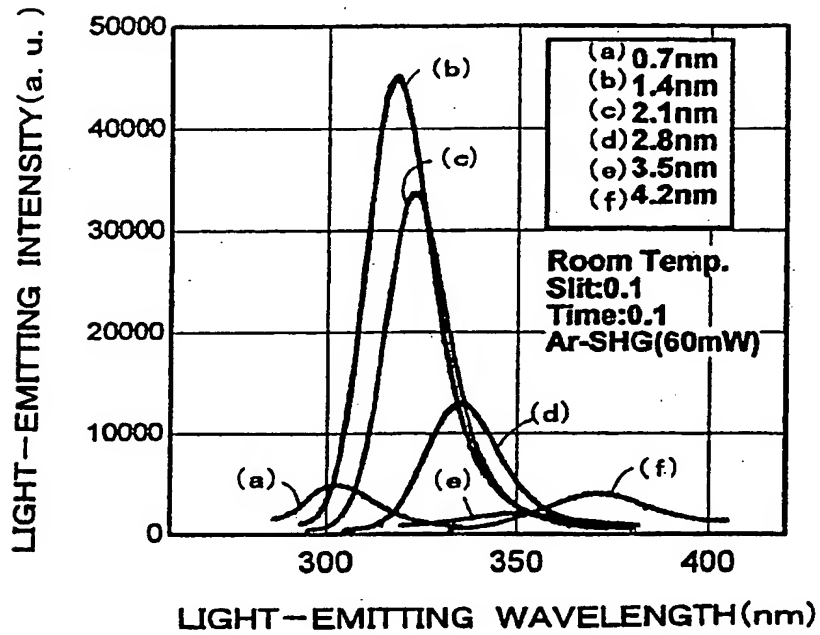
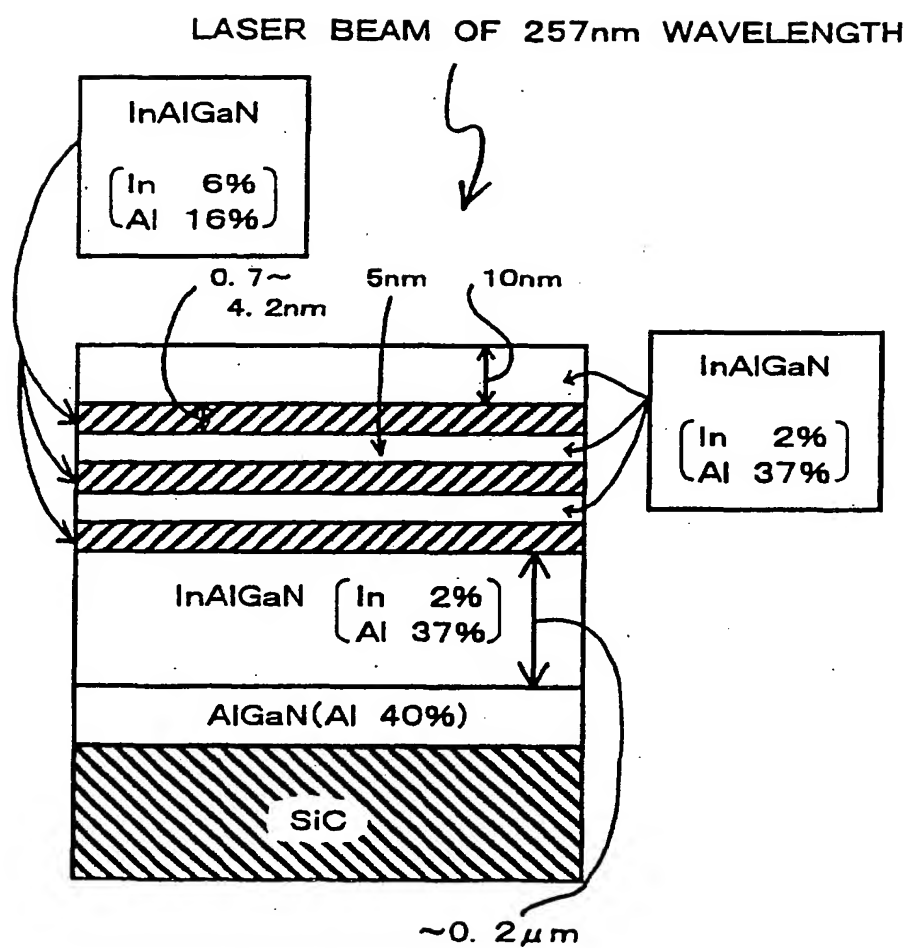


FIG. 7



(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 128 446 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
28.06.2006 Bulletin 2006/26

(51) Int Cl.:
H01L 33/00 (2006.01)

(43) Date of publication A2:
29.08.2001 Bulletin 2001/35

(21) Application number: 01301628.2

(22) Date of filing: 22.02.2001

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 23.02.2000 JP 2000045318

(71) Applicant: RIKEN
Wako-shi,
Saitama 351-0198 (JP)

(72) Inventors:
• Hirayama, Hideki
Wako-shi,
Saitama, 351-0198 (JP)
• Aoyagi, Yoshinobu
Wako-shi,
Saitama, 351-0198 (JP)

(74) Representative: Cross, Rupert Edward Blount et al
Boult Wade Tennant
Verulam Gardens
70 Gray's Inn Road
London WC1X 8BT (GB)

(54) **InAlGaN emitting light in ultraviolet short-wavelength region and process for preparing the same as well as ultraviolet light-emitting device using the same**

(57) For the purpose of emitting light in an ultraviolet short-wavelength region having a wavelength of 360 nm or shorter, it is arranged in InAlGaN in such that a ratio of composition of In is 2% to 20%, a ratio of composition

of Al is 10% to 90%, and a total of ratios of composition in In, Al, and Ga is 100%.

EP 1 128 446 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 30 1628

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	AUMER M E ET AL: "High optical quality AlInGa _N by metalorganic chemical vapor deposition" APPLIED PHYSICS LETTERS, AIP, AMERICAN INSTITUTE OF PHYSICS, MELVILLE, NY, US, vol. 75, no. 21, 22 November 1999 (1999-11-22), pages 3315-3317, XP012024104 ISSN: 0003-6951 * abstract * * page 3315, columns 1,2, paragraph 1-5 * * page 3316, column 1, paragraph 1 * * page 3316, columns 1-2, paragraph 3 * * page 3317, column 1, lines 2-16, paragraph 1; figure 4 * * page 3317, columns 1,2, paragraph 3 *	1-6	INV. H01L33/00
X	US 5 828 684 A (VAN DE WALLE ET AL) 27 October 1998 (1998-10-27) * abstract; figures 5,6 * * column 2, lines 31-38 * * column 4, lines 1-27; figure 3 * * column 5, lines 29-43 * * column 7, lines 11-24; figure 6 *	1,2,5,6	TECHNICAL FIELDS SEARCHED (IPC) H01L
X	EP 0 742 622 A (MITSUBISHI CABLE INDUSTRIES, LTD) 13 November 1996 (1996-11-13) * page 3, column 4 *	1,2,5,6	
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 480 (E-1603), 8 September 1994 (1994-09-08) -& JP 06 164055 A (ASAHI CHEM IND CO LTD), 10 June 1994 (1994-06-10) * abstract; figure 3 *	1,2,5,6	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 24 May 2006	Examiner Tinjud, F
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document</p>			

6
EPO FORM 1503 (3.02) (PSC001)

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 01 30 1628

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-05-2006

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5828684	A	27-10-1998	NONE	
EP 0742622	A	13-11-1996	NONE	
JP 06164055	A	10-06-1994	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82